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An organoindium compound with a In-Se bond, $[(Me_3CCH_2)_2InSePh]_2$, has been synthesized, characterized by elemental analyses, IR, ^1H NMR and ^{13}C NMR spectroscopies, cryoscopic molecular weight studies and an X-ray structural study. The dimeric molecule crystallizes in the centrosymmetric monoclinic spacegroup $P2_1/c$ (No. 14) with $\underline{a}$ = 18.973(4)Å, $\underline{b}$ = 10.105(1)Å, $\underline{c}$ = 19.998(6)Å, $\underline{\beta}$ = 103.66(2)°, V = 3725.4(14)Å^3, and Z = 4. Diffraction data (Mo Kα, 2θ = 5-45°) were collected on a Siemens R3m/V automated four

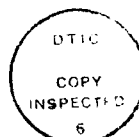| 20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
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circle diffractometer, and the structure was solved and refined to $R = 3.44\%$ and $R_W = 3.73\%$ for those 2557 unique data with $|F_o| > 6\sigma(|F_o|)$ ($R = 8.35\%$ for all 4891 data). The four-membered In_2Se_2 ring has a butterfly arrangement with the phenyl groups in the anti position relative to the ring. The In-C(neopentyl) distances range from 2.135(11)Å to 2.168(10)Å while In-Se bond distances range from 2.748(1)Å to 2.756(1)Å. There is some rotational disorder of the methyl groups within (at least) one of the neopentyl ($-CH_2CMe_3$) groups.

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21 May 1992

An Organoindium Compound Containing an Indium-

Selenium Bond: Synthesis, Properties and Molecular Structure

of [(Me$_3$CCH$_2$)$_2$InSePh]$_2$

by

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Summary: An organoindium compound with a In-Se bond, [(Me$_3$CCH$_2$)$_2$InSePh]$_2$, has

been synthesized, characterized by elemental analyses, IR, ^{1}H NMR and ^{13}C NMR

spectroscopies, cryoscopic molecular weight studies and an X-ray structural study. The

dimeric molecule crystallizes in the centrosymmetric monoclinic spacegroup P2$_1$/c (No. 14)

with $\underline{a}$ = 18.973(4)Å, $\underline{b}$ = 10.105(1)Å, $\underline{c}$ = 19.998(6)Å, $\underline{\beta}$ = 103.66(2)°, V = 3725.4(14)Å^3,

and Z = 4. Diffraction data (Mo Kα, 2θ = 5-45°) were collected on a Siemens R3m/V

automated four circle diffractometer, and the structure was solved and refined to R =

3.44% and R$_W$ = 3.73% for those 2557 unique data with $|F_o|$ > 6$\sigma(|F_o|)$ (R = 8.35% for

all 4891 data). The four-membered In$_2$Se$_2$ ring has a butterfly arrangement with the phenyl

groups in the anti position relative to the ring. The In-C(neopentyl) distances range from

2.135(11)Å to 2.168(10)Å while In-Se bond distances range from 2.748(1)Å to 2.756(1)Å. There is some rotational disorder of the methyl groups within (at least) one of the neopentyl ($-CH_2CMe_3$) groups.

Compounds of gallium and indium with bonds to the heavier group 16 elements, selenium and tellurium, have been the subject of limited research. The list of organoindium selenides includes only three compounds, $[Et_2InSe(SiEt_3)]_2$,[2] $[(i-Pr)_2InSeEt]$[3] and $[EtInSe]_n$.[2] The first two compounds in the above series were prepared by facile elimination reactions between the triorganoindium compound and the appropriate organoselenol, whereas the third compound was prepared from the first by a thermal decomposition reaction. None of the above compounds were characterized by an X-ray structural study.

An organometallic indium-selenium compound, $(Me_3CCH_2)_2InSePh$, which is not a simple adduct has been prepared by a stoichiometric ligand redistribution reaction between $In(SePh)_3$ and $In(CH_2CMe_3)_3$ in pentane at room

$$In(SePh)_3 \ + \ 2\ In(CH_2CMe_3)_3 \ \xrightarrow[\ 25°\ ]{C_5H_{12}} \ 3(Me_3CCH_2)_2InSePh$$
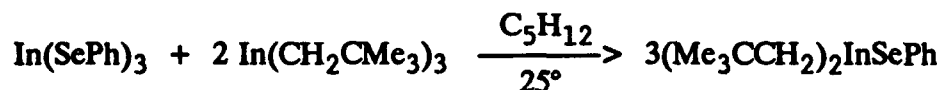
temperature. This reaction avoids the use of phenylselenol, an unpleasant smelling compound. The reagent $In(SePh)_3$ was readily prepared from indium metal and diphenyl diselenide in refluxing toluene.[4] The new compound $(Me_3CCH_2)_2InSePh$ has been fully characterized by partial elemental analyses (C and H), physical properties, infrared

spectroscopy, ^{1}H NMR and ^{13}C NMR spectroscopy, cryoscopic molecular weight studies in benzene and an X-ray structural study.

The unit cell contains four dimeric molecules of $[(Me_3CCH_2)_2InSePh]_2$. The molecules possess no crystallographic symmetry and are mutually separated by normal van der Waals' distances. There are no anomalously short intermolecular contacts. The labeling of the atoms in the molecule is shown in Figure 1. Selected interatomic distances and angles are collected in Tables I and II. Crystals of this indium-selenium compound are isomorphous with those of $[(Me_3CCH_2)_2GaTePh]_2$.[5] These two compounds have very similar unit cell parameters and structural features, including abnormally large thermal ellipsoids representing terminal carbon atom positions on the neopentyl ligands. Corrections were made for these large thermal ellipsoids in $[(Me_3CCH_2)_2InSePh]_2$ by using a *disordered model*. However, the gallium-phenyltelluride structure was previously treated as an ordered system.

The In_2Se_2 core has a butterfly configuration with the following distances: In(1)-Se(3) = 2.745(2)Å, In(1)-Se(4) = 2.735(1)Å, In(2)-Se(3) = 2.756(1)Å and In(2)-Se(4) = 2.738(1)Å. The In(1)···In(2) distance is 3.746Å and the Se(3)···Se(4) distance is 3.866Å. Internal angles are Se(3)-In(1)-Se(4) = 89.7(1)°, Se(3)-In(2)-Se(4) = 89.5(1)°, In(1)-Se(3)-In(2) = 85.8(1)° and In(1)-Se(4)-In(2) = 86.4(1)°. The fold angle about the In(1)···In(2) axis, defined as the angle of intercept between the In(1)-Se(3)-In(2) plane and the In(1)-Se(4)-In(2) plane, is 149.2°. The fold angle about the Se(3)···Se(4) axis is 148.3°. One possible explanation for the fold in the four membered ring is that it acts so as to relieve steric interactions between the surrounding ligands as seen from the view of the molecule down the Se(3)···Se(4) axis (Figure 2). Note that the phenyl ligand associated with Se(4) is

located between two neopentyl ligands on the same side of the core. These two neopentyl ligands are bent away from the phenyl ring, due to the folding of the In_2Se_2 system. If the In_2Se_2 ring were forced into a planar conformation, two neopentyl ligands would be forced into locations with more severe interactions with the phenyl ring. Therefore, the fold of the molecular core seems to be caused by steric interactions between the surrounding ligands.

The formation of a non-planar, rather than planar, In_2Se_2 molecular core appears to be related to steric factors which are almost always related to interactions between the bridging ligands and substituents on the indium(III) atom. Thus, if the bridging ligand is small, we expect a planar In_2X_2 ring. This is observed for $[(Me_3CCH_2)(Me_3SiCH_2)InCl]_2$,[6] despite there being inequivalent ligands at indium. Also, if the bridging ligand has a two-fold symmetry element (either a C_2 axis or a mirror plane) which <u>could</u> be coincident with a potential equivalent axis in the M_2X_2 system, then we will probably observe a planar In_2X_2 ring. In this case, bending the In_2X_2 system will typically relieve interactions on the opened side of the ring and simultaneously increase interactions on the closed side of the ring. Thus, $[(Me_3SiCH_2)_2InP(SiMe_3)_2]_2$,[7] $[(Me_3SiCH_2)_2InAs(SiMe_3)_2]_2$,[8] and $[(Me_3SiCH_2)_2InPPh_2]_2$[9] each have planar In_2P_2 or In_2As_2 rings.

The non-planarity of $[(Me_3CCH_2)_2InSePh]_2$ has been explained above (note that the SePh ligand itself has no appropriate symmetry axis). Species with non-equivalent bridging ligands are more difficult to analyze. Thus, the InAsInCl ring in $(Me_2SiCH_2)_2InAs(SiMe_3)_2In(CH_2SiMe_3)_2Cl$[8] is planar, whereas the InPInCl bridge in $(Me_3SiCH_2)_2InP(SiMe_3)_2In(CH_2SiMe_3)_2Cl$[7] is bent. In this case it appears that the longer In-As vs In-P distances (In-As = 2.677(1)Å; In-P = 2.601(3)-2.605(2)Å) reduce

interactions about the InAsInCl ring, relative to the InPInCl ring, enabling it to remain planar. We should also note that extending these generalizations to Ga_2X_2 systems must also take into account the smaller radius of Ga(III) versus In(III).

Each selenium atom has one phenyl group bonded to it in the trans configuration. Some relevant distances are Se(3)-C(31) = 1.934(9)Å and Se(4)-C(41) = 1.917(9)Å, while the angles of interest are In(1)-Se(3)-C(31) = 107.1(3)°, In(2)-Se(3)-C(31) = 103.7(2)°, In(1)-Se(4)-C(41) = 107.2(3)° and In(2)-Se(4)-C(41) = 100.1(3)°. The orientations of the phenylselenide ligands can be seen in Figure 3. Each selenium atom has approximately sp^3 hybridization with the lone pairs of electrons occupying sites trans to one another across the ring. The planes defined by the two phenyl rings are mutually perpendicular.

Each indium atom is linked to two neopentyl ligands with In(1)-C(10) = 2.163(10)Å, In(1)-C(15) = 2.169(10)Å, In(2)-C(20) = 2.159(9)Å and In(2)-C(25) = 2.135(11)Å. Interligand angles are C(10)-In(1)-C(15) = 131.8(4) and C(20)-In(2)-C(25) = 135.4(4). These interligand angles are substantially smaller than in the chloro-bridged indium dimer [(CH$_2$CMe$_3$)(CH$_2$SiMe$_3$)InCl]$_2$, which has interligand angles of 148.1(9)°.[6] This effect could be attributed to the difference in size of the bridging ligands. The phenylselenide ligand is much more bulky than the chloride ion. Therefore, the larger the bridging ligand, the more steric repulsion between the bridging ligand and neopentyl ligands on the indium atoms.

The terminal methyl groups on the neopentyl ligands are associated with some rotational disorder. With an ordered model, there remained a large amount of residual electron density between adjacent carbon atoms of the terminal methyl groups, despite abnormally large "anisotropic thermal parameters" for these carbon atoms. This problem

was particularly severe for that neopentyl ligand containing atoms C(25)→C(29). There were three large peaks on the electron density map corresponding to the three initially defined terminal carbon atoms, but there were also three smaller but significant peaks between these positions. This second set of peaks defined an alternate conformation of terminal methyl groups about C(26) of this neopentyl ligand. The three larger peaks were labeled as C(27), C(28), and C(29) while the three smaller peaks were labeled as C(27'), C(28') and C(29'). These two sets of peaks were related to each other by an approximate two-fold rotation about the C(25)-C(26) bond. Thus, there are six "partial-atoms" arranged in a hexagon. Each atom of the minor component is approximately trans to an atom of the major component. Since the thermal ellipsoids should have approximately the same orientation, the six U_{ij}'s of the minor component were coupled to those of that major component *trans to it*. (Uncoupled refinement of these anisotropic thermal parameters proved not to be possible.) Bond lengths within the disordered neopentyl ligand are as follows: C(26)-C(27) = 1.43(4)Å, C(26)-C(28) = 1.50(3)Å, C(26)-C(29) = 1.54(3)Å, C(26)-C(27') = 1.44(5)Å, C(26)-C(28') = 1.48(5)Å and C(26)-C(29') = 1.55(3)Å. Angles at C(26) are C(27)-C(26)-C(28) = 109(2)°, C(27)-C(26)-C(29) = 107(2)°, C(28)-C(26)-C(29) = 104(2)°, C(27')-C(26)-C(28') = 112(3)°, C(27')-C(26)-C(29') = 113(3)°, and C(28')-C(26)-C(29') = 108(3)°. The use of this model led to statistically significant reductions in the discrepancy indices, with R(all data) being reduced from 8.85% to 8.35% and a corresponding reduction in the other indicators. "Thermal parameters" for carbon atoms of the major component in this neopentyl ligand were reduced by about 45%. The other three neopentyl ligands were associated with problems similar to those above, but alternate conformations of the terminal carbon atoms were not so obvious and these features were

not further investigated. Disorder of the neopentyl ligands can be either static or dynamic, with both causing a smearing of the electron density. If the peaks are local minima in a dynamic rotation, we have the classical "hindered rotor" problem.

The cryoscopic molecular weight studies of $(Me_3CCH_2)_2InSePh$ in benzene solution and the NMR spectroscopic data are consistent with the presence of dimeric molecules in solution. Thus, the solid phase and a solution contain molecules of the same degree of association. The NMR spectral data are consistent either with the presence of the trans isomer in solution or with a rapidly equilibrating mixture of cis and trans isomers as only one set of lines is observed for the methyl and methylene protons of the neopentyl groups and for the phenyl protons. Similar results were obtained for the ^{13}C NMR spectrum at room temperature. When a CD_2Cl_2 solution of $[(Me_3CCH_2)_2InSePh]_2$ was cooled to -80 °C, the lines broadened slightly. This change in the spectrum is probably indicative of an increase in the viscosity of the solvent rather than of a slowing of an exchange process.

EXPERIMENTAL

All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or under a purified argon atmosphere. The starting compound $In(CH_2CMe_3)_3$[10] and $In(SePh)_3$[4] were prepared and purified by literature methods. Solvents were dried by conventional procedures. Elemental analyses were performed by E + R Microanalytical Laboratory, Inc., Corona, NY. Infrared spectra of Nujol mulls between CsI plates were recorded by means of a Perkin-Elmer 683 spectrometer. The ^1H NMR spectra were recorded at 400 MHz by a Varian VXR-400 S spectrometer, or at 300 MHz by using a Varian Gemini-300 spectrometer. Proton chemical

shifts are reported in δ units (ppm) and are referenced to C_6H_6 at δ 7.15 ppm or CD_2Cl_2 at 5.32 ppm. The $^{13}C\{^1H\}$ NMR spectra were recorded at 75 MHz by using a Varian Gemini-300 spectrometer or at 101 MHz by using a Varian VXR-400 S. The proton-decoupled ^{13}C spectra are reported relative to benzene at δ 128.0 ppm or CD_2Cl_2 at 53.8 ppm. All samples for NMR spectra were contained in sealed NMR tubes. Melting points were observed in sealed capillaries. Molecular weights were measured cryoscopically in benzene solution using an instrument similar to that described by Shriver and Drezdzon.[10]

Synthesis of ((Me₃CCH₂)₂In(SePh). The reagents $In(CH_2CMe_3)_3$ (0.490 g, 1.49 mmol) and $In(SePh)_3$ (0.433 g, 0.743 mmol) were mixed in 20 mL of pentane and stirred at room temperature for 15 min. Removal of pentane provided a crude product which was recrystallized in 20 mL pentane at -30 °C. X-ray quality crystals of $(Me_3CCH_2)_2In(SePh)$ (0.621 g, 1.50 mmol, 67.4% yield based upon $In(SePh)_3$ were obtained.

(Me₃CCH₂)₂In(SePh). mp 103.8-105.5 °C. Anal. Calcd for $C_{16}H_{27}InSe$: C, 46.51; H, 6.59. Found: C, 46.64; H, 6.65. ^1H NMR (C_6D_6) δ, 1.12 (s, 18H, $InCCCH_3$), 1.47 (s, 4H, $InCH_2$), 6.94 (m, 3H, m-H and p-H of Ph), 7.59 (m, 2H, o-H of Ph). ^1H NMR (CD_2Cl_2) δ, 0.99 (s, 18H, $InCCCH_3$), 1.23 (s, 4H, $InCH_2$), 7.22 (m, 3H, m-H and p-H of Ph), 7.44 (m, 2H, o-H of Ph). $^{13}C\{^1H\}$ NMR (C_6D_6) δ, 33.1 ($InCH_2\underline{C}Me$), 35.1 ($InCC\underline{C}H_3$), 40.5 ($InCH_2$), 127.3 (p-C of Ph), 129.7 (m-C of Ph), 136.2 (o-C of Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ, 33.1 ($InCH_2\underline{C}Me$), 34.9 ($InCC\underline{C}H_3$), 40.4 ($InCH_2$), 127.2 (p-C of Ph), 129.7 (m-C of Ph), 136.1 (o-C of Ph). IR(Nujol mull, cm^{-1}) 1569 (m), 1431 (m), 1358 (m), 1293 (vw), 1232 (s, sh), 1112 (m), 1090 (m), 1065 (m), 1018 (m), 997 (m), 729 (vs), 701 (m), 784 (s), 661 (m), 588 (m), 460 (m), 447 (vw), 378 (vw). Cryoscopic molecular weight, formula

weight 413.17 (obsd molality, obsd mol wt, association): 0.0426, 800.1, 1.94; 0.0298, 797,8, 1.93; 0.0195, 852.3, 2.06.

Collection of X-Ray Diffraction Data for [(Me$_3$CCH$_2$)$_2$InSePh]$_2$. The crystal selected for the diffraction study (dimensions 0.35mm × 0.30mm × 0.30mm) was sealed into a thin-walled capillary under anaerobic conditions and was aligned on a Siemens R3m/V diffractometer. Details of the data collection appear in Table III.

The crystal belongs to the monoclinic system and crystallizes in the centrosymmetric space group P2$_1$/c (space group No. 14) as indicated unequivocally by the systematic absences h0ℓ for ℓ = 2n+1 and 0k0 for k=2n+1.

Solution and Refinement of the Structure. All crystallographic calculations were carried out with the use of the Siemens SHELXTL PLUS[12] program set. The analytical scattering factors for neutral atoms were corrected for both $\Delta f'$ and i$\Delta f''$ components of anomalous dispersion.[13] The structure was solved by the use of direct methods. Abnormally large thermal parameters associated with the terminal carbon atoms of the neopentyl ligands were interpreted as due to some form of rotational disorder associated with the neopentyl ligands as discussed above. Positional and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were not located directly, but were input in calculated positions with d(C-H) = 0.96Å[14] and with the appropriate staggered tetrahedral geometry. The isotropic thermal parameter of each hydrogen was defined as equal to the U$_{eq}$ value of that carbon atom to which it was bonded. Following refinement, the extreme features left on the difference-Fourier map were a peak of height 0.66eÅ^{-3} and a negative feature of -0.63eÅ^{-3}. Refinement of the model converged with R = 3.44% and R$_w$ = 3.73% for 336 parameters refined against

those 2557 reflections with $|F_o| > 6\sigma|F_o|$ and R = 8.35% for all data. Final atomic coordinates appear in Table IV.

Supplementary Material Available. Anisotropic thermal parameters, calculated positions for hydrogen atoms, and an F_o/F_c list (_ _ pages). Ordering information is given on any current masthead page.

Figure 1

Labeling of atoms in $[(Me_3CCH_2)_2InSePh]_2$.

Figure 2

The $[(Me_3CCH_2)_2InSePh]_2$ molecule, viewed down the Se(3)···Se(4) axis.

Figure 3

The $[(Me_3CCH_2)_2InSePh]_2$ molecule, showing the relative orientation of the μ-phenylselenide ligands. (Only the major conformation of the methyl groups about C(26) is shown.)

Fig. 1
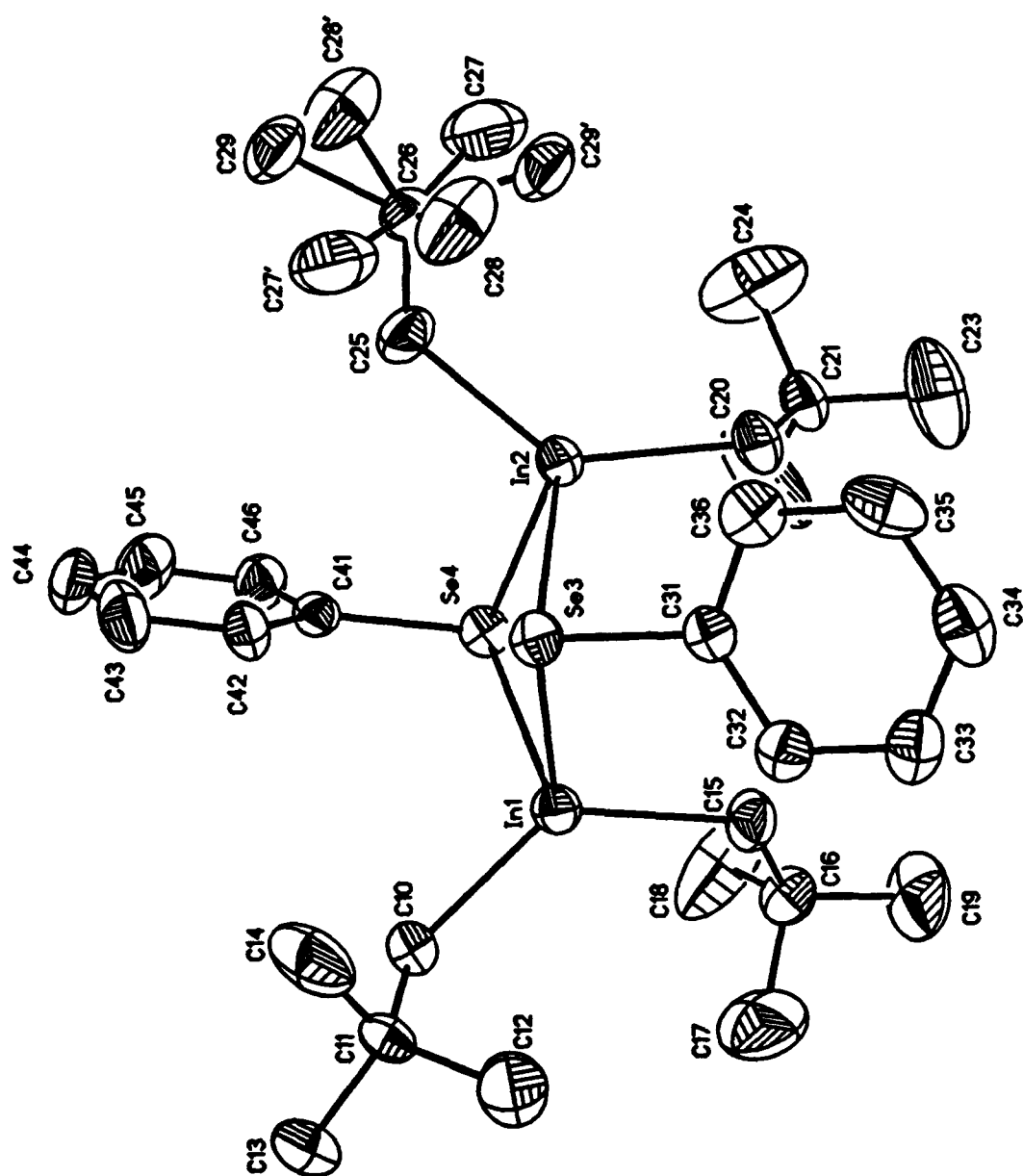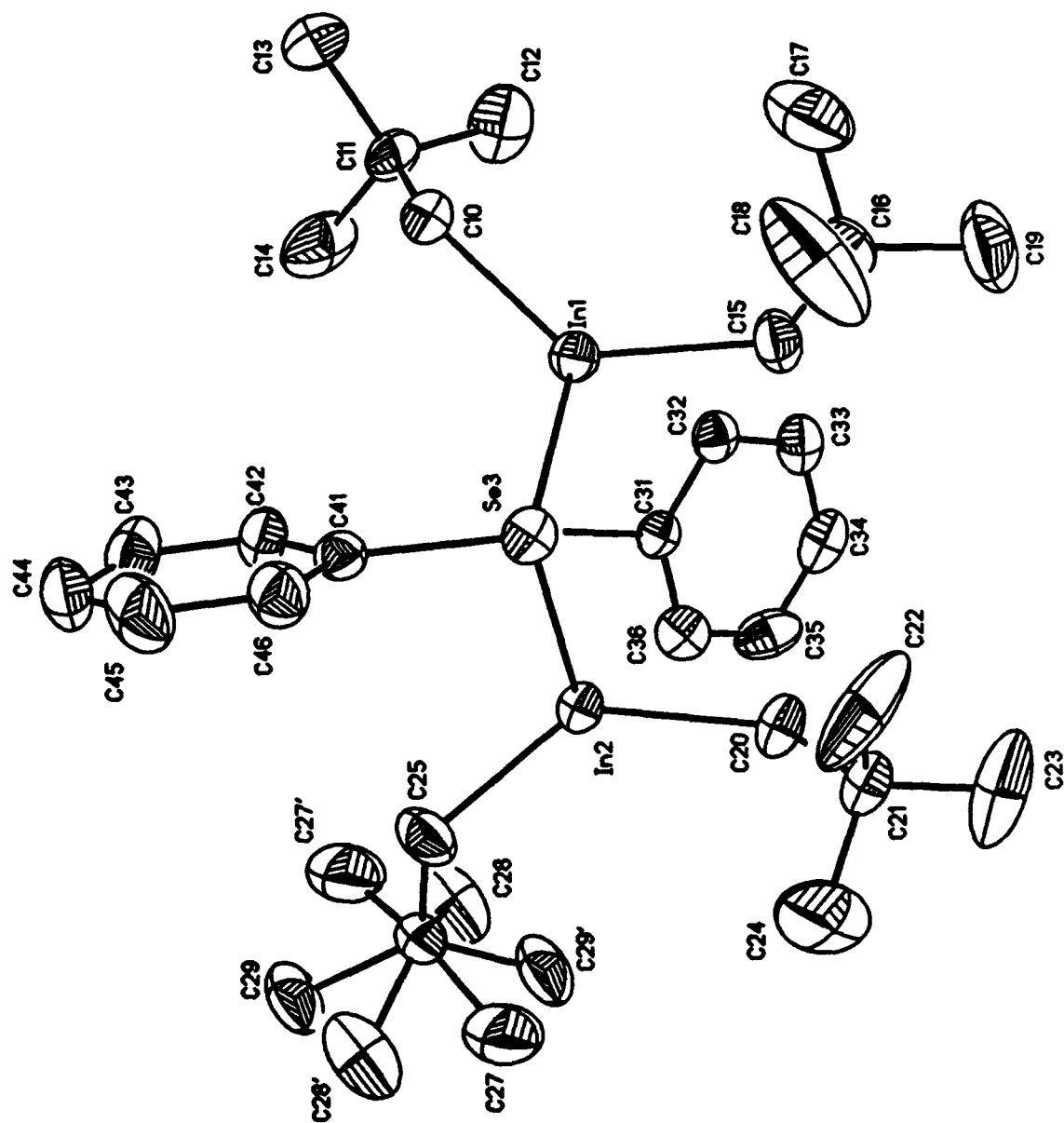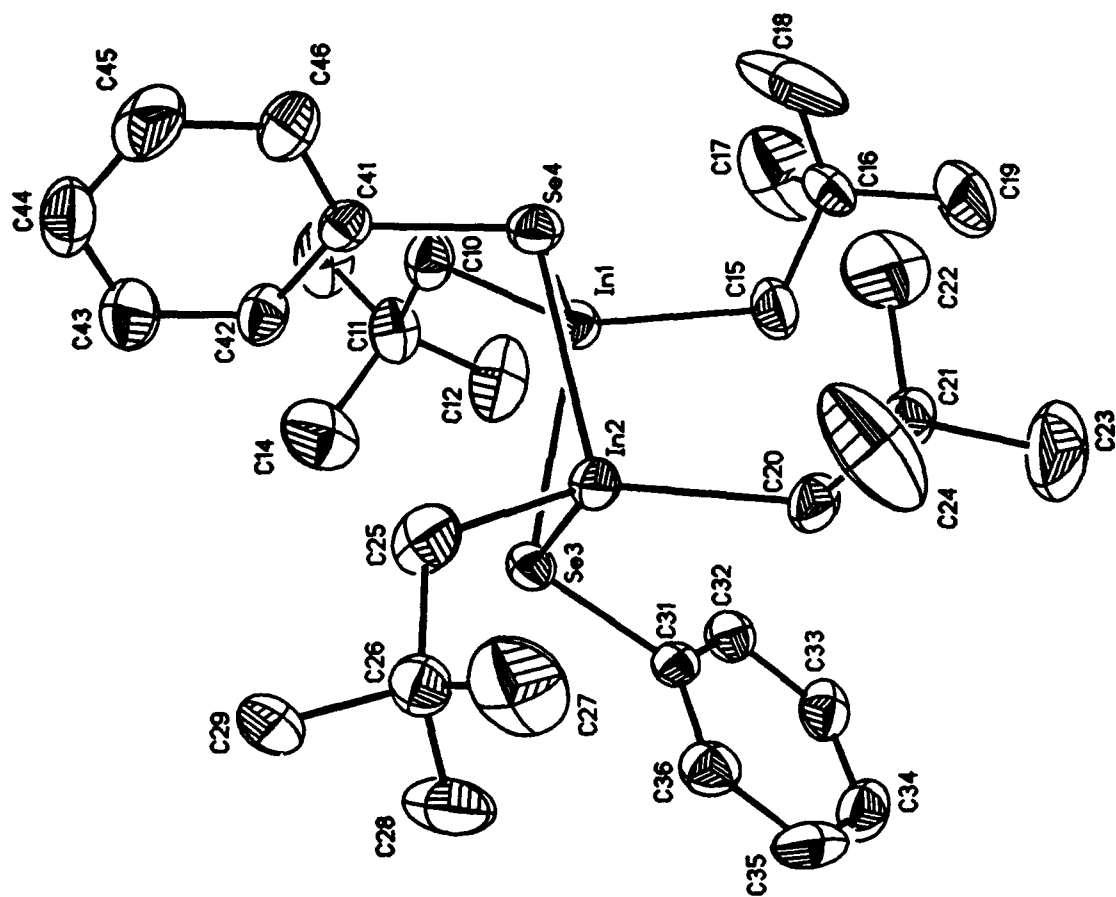
Fig 3

Table I. Bond lengths (Å)

In(1)-Se(3)	2.745	(2)	In(1)-Se(4)	2.735	(1)
In(1)-C(10)	2.163	(10)	In(1)-C(15)	2.169	(10)
In(2)-Se(3)	2.756	(1)	In(2)-Se(4)	2.738	(1)
In(2)-C(20)	2.159	(9)	In(2)-C(25)	2.135	(11)
Se(3)-C(31)	1.934	(9)	Se(4)-C(41)	1.917	(9)
C(10)-C(11)	1.516	(15)	C(11)-C(12)	1.513	(17)
C(11)-C(13)	1.499	(17)	C(11)-C(14)	1.53	(2)
C(15)-C(16)	1.508	(17)	C(16)-C(17)	1.48	(2)
C(16)-C(18)	1.45	(2)	C(16)-C(19)	1.476	(18)
C(20)-C(21)	1.499	(14)	C(21)-C(22)	1.465	(19)
C(21)-C(23)	1.471	(19)	C(21)-C(24)	1.47	(2)
C(25)-C(26)	1.494	(16)	C(26)-C(27)	1.43	(4)
C(26)-C(28)	1.50	(3)	C(26)-C(29)	1.54	(3)
C(26)-C(27')	1.44	(5)	C(26)-C(28')	1.48	(5)
C(26)-C(29')	1.55	(3)	C(31)-C(32)	1.366	(15)
C(31)-C(36)	1.349	(16)	C(32)-C(33)	1.409	(14)
C(33)-C(34)	1.34	(2)	C(34)-C(35)	1.35	(2)
C(35)-C(36)	1.417	(17)	C(41)-C(42)	1.363	(15)
C(41)-C(46)	1.358	(15)	C(42)-C(43)	1.346	(18)
C(43)-C(44)	1.39	(2)	C(44)-C(45)	1.34	(3)
C(45)-C(46)	1.347	(18)			

Table II. Bond angles (°)

Se(3)-In(1)-Se(4)	89.7(1)	Se(3)-In(1)-C(10)	111.6(3)
Se(4)-In(1)-C(10)	108.0(3)	Se(3)-In(1)-C(15)	105.8(3)
Se(4)-In(1)-C(15)	101.5(3)	C(10)-In(1)-C(15)	131.8(4)
Se(3)-In(2)-Se(4)	89.5(1)	Se(3)-In(2)-C(20)	103.2(3)
Se(4)-In(2)-C(20)	107.7(3)	Se(3)-In(2)-C(25)	107.8(3)
Se(4)-In(2)-C(25)	104.0(3)	C(20)-In(2)-C(25)	135.4(4)
In(1)-Se(3)-In(2)	85.8(1)	In(1)-Se(3)-C(31)	107.1(3)
In(2)-Se(3)-C(31)	103.7(2)	In(1)-Se(4)-In(2)	86.4(1)
In(1)-Se(4)-C(41)	107.2(3)	In(2)-Se(4)-C(41)	100.1(3)
In(1)-C(10)-C(11)	121.1(7)	C(10)-C(11)-C(12)	112.0(9)
C(10)-C(11)-C(13)	109.8(9)	C(12)-C(11)-C(13)	110.7(11)
C(10)-C(11)-C(14)	107.0(10)	C(12)-C(11)-C(14)	108.1(10)
C(13)-C(11)-C(14)	109.1(10)	In(1)-C(15)-C(16)	120.4(7)
C(15)-C(16)-C(17)	109.3(12)	C(15)-C(16)-C(18)	112.1(12)
C(17)-C(16)-C(18)	106.2(13)	C(15)-C(16)-C(19)	112.9(10)
C(17)-C(16)-C(19)	102.6(12)	C(18)-C(16)-C(19)	113.0(13)
In(2)-C(20)-C(21)	121.0(6)	C(20)-C(21)-C(22)	112.6(10)
C(20)-C(21)-C(23)	112.5(10)	C(22)-C(21)-C(23)	107.4(13)
C(20)-C(21)-C(24)	108.9(11)	C(22)-C(21)-C(24)	106.1(13)
C(23)-C(21)-C(24)	109.1(12)	In(2)-C(25)-C(26)	121.5(7)
C(25)-C(26)-C(27)	107(2)	C(25)-C(26)-C(28)	116(2)
C(27)-C(26)-C(28)	109(2)	C(25)-C(26)-C(29)	113.5(11)
C(27)-C(26)-C(29)	107(2)	C(28)-C(26)-C(29)	104(2)
C(25)-C(26)-C(27')	95(3)	C(25)-C(26)-C(28')	114(2)
C(27')-C(26)-C(28')	112(3)	C(25)-C(26)-C(29')	114(2)
C(27')-C(26)-C(29')	113(3)	C(28')-C(26)-C(29')	108(3)
Se(3)-C(31)-C(32)	120.6(7)	Se(3)-C(31)-C(36)	117.9(8)
C(32)-C(31)-C(36)	121.3(9)	C(31)-C(32)-C(33)	118.7(10)
C(32)-C(33)-C(34)	120.4(12)	C(33)-C(34)-C(35)	120.8(12)
C(34)-C(35)-C(36)	119.8(12)	C(31)-C(36)-C(35)	119.1(12)
Se(4)-C(41)-C(42)	124.2(7)	Se(4)-C(41)-C(46)	118.7(8)
C(42)-C(41)-C(46)	117.1(9)	C(41)-C(42)-C(43)	123.1(11)
C(42)-C(43)-C(44)	118.1(14)	C(43)-C(44)-C(45)	119.0(13)
C(44)-C(45)-C(46)	121.2(14)	C(41)-C(46)-C(45)	121.4(12)

Table III. Experimental Data for X-Ray Diffraction Study on [(Me$_3$CCH$_2$)$_2$InSePh]$_2$

A. Crystal Data

Empirical Formula	C$_{32}$ H$_{54}$ In$_2$ Se$_2$
Crystal System	Monoclinic
Space Group	P2$_1$/c
Unit Cell Dimensions	$\underline{a}$ = 18.973(4) Å
	$\underline{b}$ = 10.105(1) Å
	$\underline{c}$ = 19.998(6) Å
	β = 103.66(2)°
Volume	3725.4(14) Å^3
Z	4
Formula weight	826.3
Density(calc.)	1.473 Mg/m^3
Absorption Coefficient	2.995 mm^{-1}
F(000)	1648

B. Data Collection

Diffractometer Used	Siemens R3m/V
Radiation	Mo Kα (λ = 0.71073 Å)
Temperature (K)	298
Monochromator	Highly oriented graphite crystal
2θ Range	5.0 to 45.0°
Scan Type	2θ-θ
Scan Speed	Constant; 2.00°/min. in ω
Scan Range (ω)	0.45° plus Kα-separation
Background Measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard Reflections	3 measured every 97 reflections
Index Ranges	$0 \leq h \leq 20, 0 \leq k \leq 10$ $-21 \leq \ell \leq 20$
Reflections Collected	5411
Independent Reflections	4891 (R_{int} = 0.86%)
Observed Reflections	2557 (F > 6.0σ(F))
Absorption Correction	Semi-empirical
Min./Max. Transmission	0.4464 / 0.5698

C. Solution and Refinement

System Used	Siemens SHELXTL PLUS (VMS)
Solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\Sigma w(F_o-F_c)^2$
Hydrogen Atoms	Riding model, fixed isotropic U
Weighting Scheme	$w^{-1} = \sigma^2(F) + 0.0016F^2$
Number of Parameters refined	336
R Indices (all data)	R = 8.35%, wR = 6.43%
R Indices (6.0 σ)	R = 3.44%, wR = 3.73%
Goodness-of-Fit	0.89
Largest and Mean Δ/σ	0.007, 0.003
Data-to-Parameter Ratio	14.6:1
Largest Difference Peak	0.66 eÅ^{-3}
Largest Difference Hole	-0.63 eÅ^{-3}

Table IV. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$)

	x	y	z	U(eq)
In(1)	2697(1)	401(1)	7394(1)	68
In(2)	2117(1)	2307(1)	8779(1)	64
Se(3)	2364(1)	-344(1)	8603(1)	67
Se(4)	1915(1)	2677(1)	7390(1)	71
C(10)	2139(6)	-809(11)	6541(5)	88
C(11)	2203(6)	-2304(10)	6566(6)	90
C(12)	2971(7)	-2754(12)	6875(8)	148
C(13)	1934(7)	-2866(14)	5857(7)	146
C(14)	1721(9)	-2801(12)	7027(7)	153
C(15)	3800(5)	1143(12)	7680(5)	94
C(16)	4158(6)	1680(13)	7139(6)	93
C(17)	4238(10)	599(19)	6660(10)	214
C(18)	3725(9)	2693(18)	6722(11)	250
C(19)	4916(8)	2093(16)	7423(8)	184
C(20)	3181(5)	3052(9)	9267(5)	83
C(21)	3363(6)	4489(10)	9229(6)	82
C(22)	3276(12)	4951(15)	8520(8)	234
C(23)	4110(9)	4794(16)	9602(9)	211
C(24)	2858(11)	5273(13)	9520(12)	240
C(25)	1055(5)	2502(13)	8954(6)	107
C(26)	923(6)	2396(11)	9659(6)	79
C(27)	1156(21)	3617(34)	10001(17)	190
C(28)	1290(16)	1267(33)	10092(15)	156
C(29)	118(11)	2238(33)	9662(12)	134
C(27')	696(33)	1034(51)	9590(28)	190
C(28')	343(26)	3285(55)	9779(23)	156
C(29')	1607(18)	2616(58)	10250(18)	134
C(31)	3271(5)	-684(8)	9261(5)	60
C(32)	3835(6)	-1268(9)	9058(5)	75
C(33)	4469(6)	-1579(10)	9561(7)	92
C(34)	4510(8)	-1319(12)	10228(8)	106
C(35)	3944(9)	-766(12)	10429(6)	107
C(36)	3302(7)	-445(10)	9931(6)	89
C(41)	910(5)	2217(10)	7090(4)	66
C(42)	628(6)	1024(11)	7210(5)	81
C(43)	-83(8)	733(16)	7007(7)	121
C(44)	-552(7)	1708(20)	6665(8)	128
C(45)	-276(8)	2881(17)	6538(7)	128
C(46)	438(6)	3140(12)	6751(6)	95

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

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